Mixed bismuth oxides with layer lattices

I. The structure type of $CaNb_2Bi_2O_9$

By Bengt Aurivillius

With 5 figures in the text

In the course of a comprehensive investigation of mixed bismuth oxides, the system $Bi_2O_3 - TiO_2$ was studied. At about 40 atomic % of TiO_2 a phase with a body-centered pseudo-tetragonal unit cell with $a = 3.84$ and $c = 32.8$ Å was found. X-ray analysis (to be published later) seemed to show that the structure was built up of $Bi_2O_2^{2+}$ layers paralell to the basal plane, and sheets of composition $Bi_2Ti_3O_{10}^{2-}$. The atomic arrangement within the $Bi_2Ti_3O_{10}^{2-}$ sheets seemed to be the same as in structures of the perowskite type and the structure could then be described as consisting of $Bi_2O_2^{2+}$ layers between which double perowskite layers are inserted.

An attempt was then made to synthesize compounds where the $Bi_2O_2^{2+}$ layers alternate with single perowskite layers. The general formula for such compounds could be expected to be: $(MeBi)_6R_4O_{18}$. In actual fact compounds with this structure could be prepared with Me: Na K Ca Ba Sr Pb R: Ti Nb Ta.

Procedure: Weighed amounts of the appropriate oxides or carbonates were mixed and heated in platinum or gold crucibles to about 1000° C. A number of compounds with the general formula $(Bi, Me)_6R_4O_{18}$ were prepared. Out of these the following were found to have a body-centered tetragonal or pseudo-tetragonal unit cell. The real unit cells, however, appeared to be face-centered-orthorhombic.

Composition	Orthorhombic description			Pseudo-tetragonal description	
	a	b	c	a	c
Bi_3NbTiO_9	5.405	5.442	25.11	3.836	25.11
Bi_3TaTiO_9	5.402	5.436	25.15	3.832	25.15
$CaBi_2Nb_2O_9$	5.435	5.485	24.87	3.860	24.87
$SrBi_2Nb_2O_9$	5.504	5.504	25.05	3.892	25.05
$SrBi_2Ta_2O_9$	5.509	5.509	25.06	3.895	25.06
$BaBi_2Nb_2O_9$	5.533	5.533	25.55	3.912	25.55
$PbBi_2Nb_2O_9$	5.492	5.503	25.53	3.887	25.53
$KBi_5Nb_4O_{18}$	5.506	5.506	25.26	3.893	25.26
$NaBi_5Nb_4O_{18}$	5.47	5.47	26.94	3.87	26.94

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Single crystals were prepared from the $PbBi_2Nb_2O_9$ and Bi_3NbTiO_9 phases. Weissenberg photographs of $0kl$ and $1kl$ (pseudo-tetragonal cell) were taken. In the powder photographs of Bi_3NbTiO_9 (Table 6a) the reflections 110, 211, 215, 220 and 310 were clearly split up. No cleavage was found for the reflections $10l$, $20l$, and $30l$, (in all cases pseudo-tetragonal indices). From this it was concluded that the structure might be described by means of orthorhombic unit cells, having the same c axes as the pseudo-tetragonal cells, and a and b axes equal to the diagonals of the pseudo-tetragonal cells. Using orthorhombic units the Weissenberg photographs register hhl and $h, h+2, l$. In Table 6a the $\sin^2 \theta$ of Bi_3NbTiO_9 are calculated on the assumption of an orthorhombic unit cell.

A few discrepancies occur between the intensities of the spots as found in the Weissenberg photographs (first layer) and in the powder photographs. In the Weissenberg photographs $(h, h+2, l)$, no difference was found between reflections hkl and khl. From the powder photographs it is seen that 024 might be < 204 and that $311 < 131$ and $31\ 11 < 13\ 11$. The reason might be the orientation of the powder.

$PbBi_2Nb_2O_9$ phase

The powder photographs of $PbBi_2Nb_2O_9$ (Table 6b) could be explained assuming a tetragonal cell with $a = 3.887$ Å and $c = 25.53$ Å, but for two lines being split up, which indicated an orthorhombic unit cell with axes $a = 5.492$, $b = 5.503$ and $c = 25.53$ Å. As in Bi_3NbTiO_9, it was thus assumed that the real symmetry is $D_{2h}-mmm$, though nothing in the Weissenberg photographs indicated a lower Laue symmetry than $D_{4h}-4/mmm$. The observed density was 7.91, thus allowing 4 formula units/unit cell ($d_{calc.} = 8.22$).

With the exception of the criterion for face-centering that hkl occuring only with h, k, l all odd or all even, no systematic extinctions were found. This is characteristic of the space groups D_{2h}^{23}, D_2^7 and C_{2v}^{18}.

Positions of the metal atoms

As the scattering factors for the Pb and the Bi atoms are almost the same, it makes no difference in the intensity calculations whether the Pb and the Bi atoms occupy separate positions or are mixed at random. Therefore no difference will be made between Pb and Bi; they will both be denoted by Me. The intensities of the reflections seemed to depend mainly on the value of l (see Table 1a). It therefore seemed probable that at least the Me and the Nb atoms are placed along the lines: $(000;\ \frac{1}{2}\frac{1}{2}0;\ \frac{1}{2}0\frac{1}{2};\ 0\frac{1}{2}\frac{1}{2}) + 00z$. The sum of $\sum_l I_{00l} \cos 2\pi lz$ and $\sum_l I_{11l} \cos 2\pi lz$ will under such conditions represent the Patterson function along $00z$. In Fig. 1a these sums are plotted as functions of z. It is seen from the graph that high maxima occur for $z = 0.20$ and $z = 0.40$.

The unit cell of $PbBi_2Nb_2O_9$ contains 12 Me atoms and 8 Nb atoms.

If the space groups are assumed to be D_{2h}^{23}, D_2^7 or C_{2v}^{18} a or b, the only way of placing 12 Me atoms on the lines $00z$ is in one 4-fold and one 8-fold position. With these assumptions the only 4-fold positions possible are 000 or $00\frac{1}{2}$

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Table 1a

Weissenberg Photographs of $PbBi_2Nb_2O_9$. Cu K_α radiation

The crystals form very thin plates, and therefore considerable absorption occurs. Spots in the vicinity of the lines described by WELLS (2) will therefore be weakened. The regions of maximum absorption are denoted by dotted lines. In the tables 1, 2 and 3 pseudo-tetragonal indices are used, and observed and calculated intensities for the reflections: $0\,0\,l$, $1\,0\,l$, $1\,1\,l$, $2\,0\,l$, and $2\,1\,l$ are given. With orthorhombic description these reflections would have been denoted by: $0\,0\,l$, $0\,2\,l$ or $2\,0\,l$, $2\,2\,l$, $1\,3\,l$ or $3\,1\,l$.

l	I_1	I_2	I_{00l}	$\dfrac{I_{obs.}}{I_{11l}}$	I_{20l}
2	18	1.2		vw	vw
4	9.0	.34	m⁻	m	w
6	0.1	8.4	vvw	m·	—
8	25	14	m⁻	w	w⁻
10	350	340	vst	m⁺	m
12	19	0.2	w	—	—
14	36	100	m⁺	vvw	w⁻
16	9.6	4.8	vw	—	—
18	45	31	m	w	w
20	280	230	st	m⁺	m⁺
22	22	0.04	—	m	—
24	71	200	m⁺	m	m⁺
26	27	14	w	vvw	vw
28	85	26	m⁻	w	w
30	190	130	m	m	
32	25	8.4	w		

l	I_1	I_2	I_{10l}	$\dfrac{I_{obs.}}{I_{21l}}$	
1	1.7	17	m⁻	—	
3	20	6.3	m⁻	vvw	
5	380	370	vst	st	
7	18	0.0	—	—	
9	12	63	m	w	
11	3.2	5.3	—	—	
13	32	23	w	vvw	
15	320	280	st	w	
17	20	0.2	—	—	
19	55	160	m⁺	w⁺	
21	18	7.8	vvw	—	
23	61	32	m	w⁺	
25	230	170	m⁺	m	
27	24	1.7	—	—	
29	85	250	m⁺	—	
31	48	23	w		

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Table 1b
Weissenberg Photographs of $PbBi_2Nb_2O_9$

Zero layer				First layer			
$00l$	I'_1	$I_{obs.}$	I'_2	$21l$	I'_1	$I_{obs.}$	I'_2
4	11	m^-	32	1	1.7	—	14
6	1.4	vvw^-	1.4	3	18	vvw	4.8
8	28	m^-	14	5	330	st	340
10	360	vst	360	7	18	—	0.4
12	45	w	11	9	23	w	67
14	50	m^+	88	11	4.8	—	3.6
16	6.3	vw	5.8	13	26	vvw	23
18	70	m	38	15	300	w	280
20	280	st	230	17	13	—	0.3
22	25	—.	0.4	19	42	w^+	150
24	58	m^+	250	21	14	—	7.8
26	21	w.	10	23	66	w^+	36
28	85	m^-	21	25	210	m	170
30	240	m	120	27	23	—	2.9
32	17	w	6.8				
$10l$	I'_1	$I_{obs.}$	I'_2	$11l$	I'_1	$I_{obs.}$	I'_2
1	1.0	m^-	8.4	2	18	vw	1.2
3	14	m^-	4.0	4	9.0	m	34
5	320	vst	340	6	0.1	m	8.4
7	16	—	0.5	8	25	w	14
9	24	m	67	10	350	m^+	340
11	6.3	—	2.0	12	19	—	0.2
13	24	w	24	14	36	vvw	100
15	310	st	280	16	9.6	—	4.8
17	13	—	0.5	18	45	w	31
19	42	m^+	150	20	280	m^+	230
21	14	vvw	7.8	22	22	—	0.0
23	64	m	38	24	71	m	200
25	210	m	170	26	27	vvw	14
27	23	—	2.9	28	85	w	26
29	81	m^+	220	30	190	m	130
31	32	w	24				
$20l$	I'_1	$I_{obs.}$	I'_2				
2	12	vw	1.4				
4	10	w	36				
6	0.5	—	4.8				
8	31	w^-	14				
10	350	m	350				
12	41	—	7.8				
14	50	w^-	88				
16	6.3	—	6.3				
18	69	w	40				
20	280	m^+	230				
22	25	—	0.4				
24	59	m^+	240				
26	20	vw	11				
28	85	w	21				

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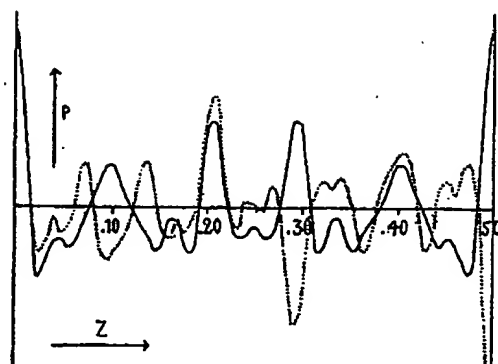
Figure 1 a. Patterson function of $Pbv_2Bi_2Nb_2O_9$ along $00z$

Full curve: $\sum_l I_{00l} \cos 2\pi l z$

Dotted curve: $\sum_l I_{11l} \cos 2\pi l z$ (orthorhombic indices).
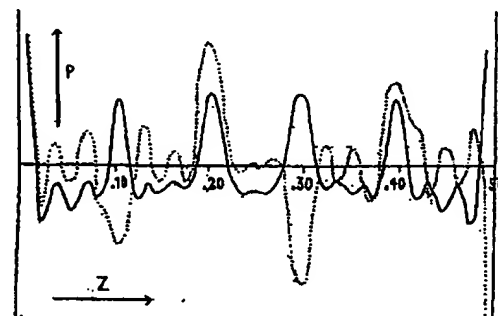
Figure 1 b. Patterson function of Bi_3NbTiO_9 along $00z$

Of 8-fold positions only $\pm 00z$ is possible.

It was assumed arbitrarily that 4 Me occupy the position 000.

Using the distances found with the aid of the Patterson function, two possibilities for placing the Nb atoms arose:

1. 8 Nb in $\pm$ 00 0.20   4 Me in 000   8 Me in $\pm$ 00 0.40
2. 8 Nb in $\pm$ 00 0.40   4 Me in 000   8 Me in $\pm$ 00 0.20

The two curves on the graph were added and the areas under the peaks at 0.20 and 0.40 calculated. The ratio 1.5 : 1 was found for 0.20/0.40.

In case 1, the ratio was calculated to be 0.91 : 1 and in case 2, 1.1 : 1 if the ratio f_{Nb}/f_{Bi} was assumed to be 0.46. These figures cannot be compared directly with the observed ratio 1.5 : 1 since the zero level in figure 1 is of course uncertain. Case 2 agrees slightly better insofar as the peak at 0.20 is actually higher. It seemed, however, that the uncertainty in determining the areas was so large that case 1 could not be excluded by these measurements alone.

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Case 1

In calculating the structure amplitudes z_{Nb} was varied around 0.20 and z_{Mo} around 0.40. The average ratio f_{Nb}/f_{Mo} was assumed to be 0.46. The intensities were compared with calculated values of A^2:

$$A = 10 \,(\cos 2\pi l z_{Mo} + 0.46 \cos 2\pi l z_{Nb} + 0.5) = 10 \, F/4 \, f_{Mo}.$$ In this way the best values for the parameters were found to be:

$z_{Mo} = 0.397 \pm 0.002$ and $z_{Nb} = 0.192 \pm 0.004$. In Table 1a $I_{calc.}$ is compared with the observed intensities.

Case 2

z_{Nb} was varied about 0.40 and z_{Mo} around 0.20. The best values were found to be $z_{Nb} = 0.412 \pm 0.004$ and $z_{Mo} = 0.202 \pm 0.002$.

The observed and calculated values are compared in Table 1a.

It was found that arrangement 2 accounted slightly better for the experimental data than 1. It must, however, be borne in mind that the intensity ratios of weak spots might be changed through the influence of the oxygen atoms and that this influence was neglected in the calculations. The differences did not seem to be as large as to allow a decision between 1 and 2. It was therefore tried to find possible oxygen positions both for 1 and 2. The results were then compared.

Case 1. Positions of the oxygen atoms

The positions of the metal atoms were assumed to be: $(0\,0\,0;\ 0\,\frac{1}{2}\,\frac{1}{2};\ \frac{1}{2}\,0\,\frac{1}{2};\ \frac{1}{2}\,\frac{1}{2}\,0) + 0\,0\,0$ (4 Me_1) $\pm\ 0\,0\ 0.397$ (8 Me_2) $\pm\ 0\,0\ 0.192$ (8 Nb). Since all point positions of D_{2h}^{23} can be described by positions of D_2^7 or $C_{2v}^{18}\,a$, only D_2^7 and $C_{2v}^{18}\,a$ have been considered.

At first only D_2^7 will be discussed. If the interatomic distances O–O, Me–O and Nb–O should not be smaller than 2.5, 2.2 and 1.8 Å. oxygen atoms could only be situated in the following positions:

$4\,(b)\ 0\,0\,\frac{1}{2}$ $4\,(c)\,\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$ $4\,(d)\ \frac{1}{4}\,\frac{1}{4}\,\frac{3}{4}$ $8\,(g)\ \pm\ 0\,0\,z$
$8\,(h)\ \frac{1}{4}\,\frac{1}{4}\,z;\ \frac{1}{4}\,\frac{1}{4}\,\frac{1}{2}-z$ $0.086 \leq z \leq 0.122$
                    $0.039 \leq |z| \leq 0.061$ $0.262 \leq z \leq 0.311$
                    $0.148 \leq |z| \leq 0.201$
$8\,(i)\ \frac{1}{4}\,y\,\frac{1}{4};\ \frac{1}{4}\,\frac{1}{4}-y\,\frac{1}{4}$ $8\,(j)\ x\,\frac{1}{4}\,\frac{1}{4};\ \frac{1}{4}-x\,\frac{1}{4}\,\frac{1}{4}$
                $y = 0$ $x = 0$

An attempt was made to find positions for the oxygen atoms giving approximately regular octahedra around Nb, since from known structures containing Nb^{5+} and O^{2-} this seemed to be the normal configuration $Nb^{5+}-O^{2-}$. The maximum distance of contact Nb–O was assumed to be 2.5 Å.

With these assumptions $8\,(g)$ and $8\,(h)$ are the only positions where oxygen atoms in contact with Nb can be situated.

With oxygen atoms in three 8-fold positions $8\,(h)$ the distances O–O would be too short. It then only remains to consider the case of oxygen atoms in two 8-fold positions $8\,(g)$ and two 8 fold positions $8\,(h)$. For the oxygen

atoms in contact with Nb, reasonable interatomic distances were obtained assuming: $8 \ O_2$ in $8(g)$ $z_2 = 0.100$ $8 \ O_3$ in $8(g)$ $z_3 = 0.264$ $8 \ O_4$ in $8(h)$ $z_4 = 0.168$ $8 \ O_5$ in $8(h)$ $z_5 = -0.168$. Even if small adjustments of these parameters are admitted for the remaining 4 O there is room only in the position $00\frac{1}{2}$ (O_1). With these assumptions the distances would be:

$Me_1 - 4 \ O_1 = 2.75$	$Me_2 - 4 \ O_2 \ 2.75$	$Nb - \ O_2 = 2.34$
$Me_1 - 2 \ O_3 = 2.55$	$Me_2 - 2 \ O_4 \ 2.55$	$Nb - 2 \ O_4 = 2.04$
	$Me_2 - 2 \ O_5 \ 2.55$	$Nb - \ O_5 = 2.04$
		$Nb - \ O_3 = 1.84$

$$O_4 - 4 \ O_5 = 2.74$$
$$O_3 - 2 \ O_4 = 2.60$$
$$O_3 - 2 \ O_5 = 2.60$$
$$O_1 - 2 \ O_2 = 2.55$$

It is seen that the positions given might equally well be described by D_{2h}^{23} or if the pseudo-tetragonal unit cell ($a = 3.89$ $c = 25.53$ Å) is chosen by D_{4h}^{17}.

As $a \sim b$ and the positions of the oxygen atoms must be chosen from space considerations, the discussion will be the same for $C_{2v}^{18}a$ as for $C_{2v}^{18}b$. For $C_{2v}^{18}a$ it is found that the oxygen atoms can be only in the planes $y = 0$ $y = 0.25 \pm 0.03$ $y = \frac{1}{2}$ and $y = 0.75 \pm 0.03$. For $y = 0$ or $\frac{1}{2}$, z must either be 0 or $\frac{1}{2}$ or lie between the limits $0.049 < |z| < 0.451$, otherwise the distance O—O will be < 2.5 Å. For $y = \frac{1}{4}$ or $\frac{3}{4}$, z must have the values 0, $\frac{1}{2}$, $\frac{1}{4}$ or $\frac{3}{4}$ or lie between the limits $0.049 < |z| < 0.201$ $0.299 < |z| < 0.451$.

In figure 2a sections of the unit cell are made for $y = 0$ and $y = \frac{1}{4}$. Possible regions with space group $C_{2v}^{18}a$ are denoted in the figure by shaded areas. For these areas the distances $O—O \geq 2.5$. $Me—O \geq 2.2$ and $Nb—O \geq 1.8$ Å.

With space group $C_{2v}^{18}a$ it thus seems that no basically new atomic positions are obtained, although this symmetry allows the atoms to be slightly shifted from the positions of D_2^7.

In Table 1 the intensities have been calculated from the parameters found and compared with the observed ones. (The calc. intensities are denoted by I_1'). The mode of calculation is shown by the calculation of I_{001}. $I = A^2$.

$A = 10 \ (0.5 + \cos 2\pi l z_{Me} + (f_{Nb}/f_{Me}) \cos 2\pi l z_{Nb} + (f_o/f_{Me}) \ (0.5 + \cos 2\pi l z_2 + + \cos 2\pi l z_3 + 2 \cos 2\pi l z_4)$. Since the ratios f_{Nb}/f_{Me} and f_o/f_{Me} vary with $\sin \theta/\lambda$ they were interpolated from values given in the *International Tables* (1).

Case 2. Positions of the oxygen atoms

The positions of the metal atoms were assumed to be: $(000; \ \frac{1}{2}\frac{1}{2}0; \ 0\frac{1}{2}\frac{1}{2}; \ \frac{1}{2}0\frac{1}{2}) +$ $+ 000 \ (4 \ Me_1) \pm 00 \ 0.202 \ (8 \ Me_2) \pm 00 \ 0.412 \ (8 \ Nb)$.

With D_2^7 the following positions are available for the oxygen atoms $4(b) \ 00\frac{1}{2}$

$8(g) \pm 00z$	$8(h) \ \frac{1}{4}\frac{1}{4}z, \ \frac{1}{4}\frac{1}{4}\frac{1}{2}-z$
$0.086 \leq z \leq 0.116$	$0.039 \leq |z| \leq 0.161$
$0.288 \leq z \leq 0.342$	

$4(c) \ \frac{1}{4}\frac{1}{4}\frac{1}{4}$ $\quad$ $4(d) \ \frac{1}{4}\frac{1}{4}\frac{3}{4}$ $\qquad$ $16(k) \ xyz, \ \bar{x}\bar{y}z, \ x\bar{y}\bar{z}, \ \bar{x}y\bar{z}$
$x = 0$ $\quad x = 0.25 \pm 0.03$
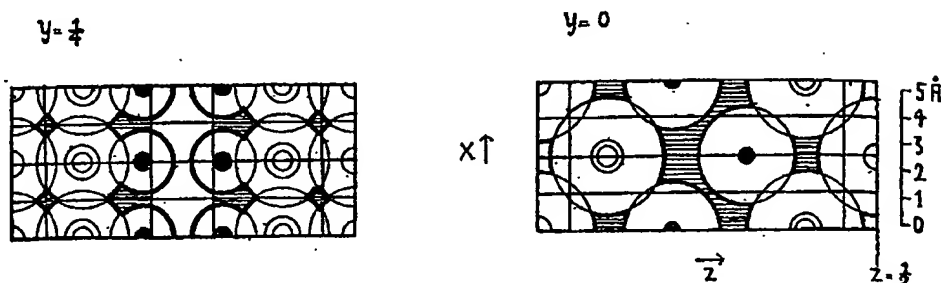$y = 0.25 \pm 03$ or $y = 0$
$z \sim 0.135$.

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$y = \frac{1}{4}$ $y = 0$

Figure 2 a (see Case 1 in the text.)

The projection of the positions of the Nb, Me_1 and Me_2 atoms on the planes $y = 0$ and $y = \frac{1}{4}$ are denoted by: black circles, white circles and double circles respectively.
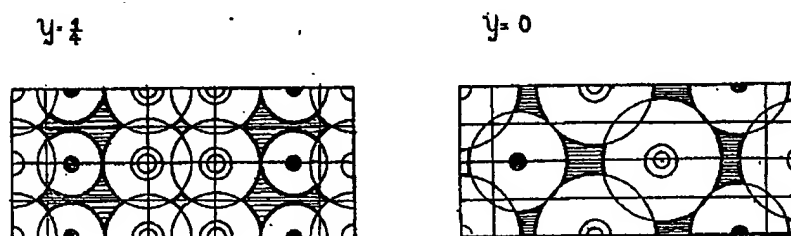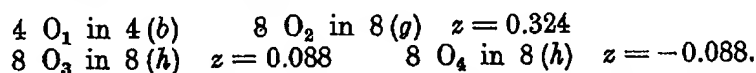
$y = \frac{1}{4}$ $y = 0$

Figure 2 b (see Case 2 in the text.)

It was found that oxygen atoms in the positions 4 (c), 4 (d) or 16 (k) could not be part of an octahedron around Nb. With O in the remaining positions, 4 (b), 8 (g) and 8 (h), octahedra around Nb might be achieved in the following ways: $(1.8 \leq Nb-O \leq 2.5)$.
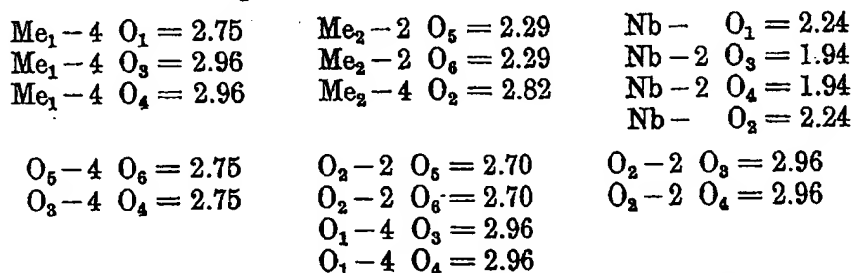
With oxygen atoms in three 8-fold positions 8 (h), it seemed impossible to find positions for the remaining 12 oxygen atoms giving O–O distances ≤ 2.5 Å.

With two 8-fold positions 8 (h) + 4 (b) + one 8-fold position 8 (g) the following positions were assumed for oxygen atoms in contact with Nb:

$$4 \; O_1 \; \text{in} \; 4 \, (b) \qquad 8 \; O_2 \; \text{in} \; 8 \, (g) \quad z = 0.324$$
$$8 \; O_3 \; \text{in} \; 8 \, (h) \quad z = 0.088 \qquad 8 \; O_4 \; \text{in} \; 8 \, (h) \quad z = -0.088.$$

For the remaining 8 oxygen atoms there was only room in the positions 4 (c) and 4 (d). (O_5, O_6).

With the above assumptions the distances would be:

$Me_1 - 4 \; O_1 = 2.75$	$Me_2 - 2 \; O_5 = 2.29$	$Nb - \quad O_1 = 2.24$
$Me_1 - 4 \; O_3 = 2.96$	$Me_2 - 2 \; O_6 = 2.29$	$Nb - 2 \; O_3 = 1.94$
$Me_1 - 4 \; O_4 = 2.96$	$Me_2 - 4 \; O_2 = 2.82$	$Nb - 2 \; O_4 = 1.94$
		$Nb - \quad O_2 = 2.24$

$O_5 - 4 \; O_6 = 2.75$	$O_2 - 2 \; O_5 = 2.70$	$O_2 - 2 \; O_3 = 2.96$
$O_3 - 4 \; O_4 = 2.75$	$O_2 - 2 \; O_6 = 2.70$	$O_2 - 2 \; O_4 = 2.96$
	$O_1 - 4 \; O_3 = 2.96$	
	$O_1 - 4 \; O_4 = 2.96$	

The above positions might be equally well described by D_{2h}^{23} or if a pseudo-tetragonal unit cell is assumed ($a = 3.89 \; c = 25.53$) by D_{4h}^{17}.

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In Figure 2 b sections are made of the unit cell for $y = 0$ and $y = \frac{1}{4}$ showing the positions possible for the oxygen atoms if the space group $C_{2v}^{18} a$ is assumed. Possible regions are denoted by shaded areas. It was found that only with oxygen atoms situated near the positions given above, could octahedra of O around all Nb atoms and reasonable distances O–O be attained.

Thus no new arrangements were found when space group $C_{2v}^{18} a$ was assumed. In Table 1 the intensities are calculated from the parameters given above. The calculated intensities are denoted by I_2'. The mode of calculation is the same as was used in case 1. It is seen from the Table that both 1 and 2, in which cases the influence of the oxygen atoms was neglected, account fairly well for the experimental data. From this follows that the calculated intensities I_1' and I_2', where regard was taken to the O atoms, do not differ much either. Although the ratio 211:213 (see Table 1 (pseudo-tetragonal indices)) is best described by $1'$, $2'$ on the whole seemed to satisfy the observed intensities best (see for instance the intensity ratios 112:114 116:118 202:204 101:103 and 107:109). No definite conclusions could however be drawn from the study of $PbBi_2NbO_9$ alone.

Bi_3NbTiO_9

Just as for $PbBi_2Nb_2O_9$, there was nothing in the Weissenberg photographs to indicate a lower Laue symmetry than D_{4h}–$4/mmm$. From the powder photographs (Table 6 a) it is however seen that the actual unit cell is orthorhombic with axes $a = 5.405$ $b = 5.442$ $c = 25.11$ Å.

The intensities of the spots in the Weissenberg photographs indicate that the metal atoms are probably placed on the lines $00z$. The Patterson function (Fig. 1 b) showed high maxima at 0.20 and 0.40. If the same assumptions are made as for $PbBi_2Nb_2O_9$ the following arrangements seemed to be possible:

A. 4 Nb in 0 0 0
   8 BiTi in $\pm$ 0 0 z_1
   8 BiTi in $\pm$ 0 0 z_2

B. 4 Ti in 0 0 0
   8 BiNb in $\pm$ 0 0 z_1
   8 BiNb in $\pm$ 0 0 z_2

C_1 4 Bi in 0 0 0
   8 NbTi in $\pm$ 0 0 z_1
   8 Bi in $\pm$ 0 0 z_2

C_2 4 Bi in 0 0 0
   8 NbTi in $\pm$ 0 0 z_2 $z_1 \sim 0.20$ $z_2 \sim 0.40$
   8 Bi in $\pm$ 0 0 z_1

The areas under the peaks at 0.20 and 0.40 were calculated as for $PbBi_2Nb_2O_9$ and the ratio 0.20/0.40 was found to be 1.4. The calculated ratios for A, B, C_1 and C_2 were 1.0, 1.0, 0.84 and 1.2. The area ratio for C_2 agreed best with the observed one. The differences are however small, so that all alternatives were considered. The intensities were calculated as for $PbBi_2Nb_2O_9$. The ratios f_{Ti}/f_{BiNb}, f_{Nb}/f_{BiTi} and f_{NbTi}/f_{Bi} were assumed to be 0.26, 0.57 and 0.34. The calculated and observed intensities for A and B are compared in Table 2. In these calculations the influence of the oxygen atoms was neglected. The best agreement was found for

	z_1	z_2
A	0.198	0.400
B	0.196	0.400

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Table 2
Weissenberg photographs of Bi_3NbTiO_9.

l	I_A	I_B	I_{00l}	$\dfrac{I_{obs.}}{I_{11l}}$	I_{20l}
2	4.0	12	—	vvw	vw
4	7.3	22	m	st	m+
6	2.3	5.3	w	st	m
8	7.3	22	m	w	m
10	510	440	st	st	st
12	1.4	2.6	w	—	vw
14	15	52	m+	vw	w
16	0.2	0.0	w	vw	—
18	11	30	m+	w	vw
20	500	400	st	st	m+
22	0.1	0.4	—	—	—
24	27	94	m	m	m
26	0.5	2.0	w	m	m
28	14	31	m	m+	m+
30	490	350	m	m+	

l	I_A	I_B	I_{10l}	I_{21l}	
1	4.4	12	st	m+	
3	5.8	17	m	vw	
5	520	450	vst	vst	
7	2.6	6.3	—	—	
9	11	35	m	m	
11	0.8	1.4	w	w	
13	9.0	27	vw	w	
15	510	420	st	w	
17	0.6	0.3	—	—	
19	20	70	w	w	
21	0.0	0.5	w	w	
23	12	31	m	m	
25	500	380	m+	m+	
27	0.0	3.2	—	—	
29	34	120	m	m	
31	1.4	4.4	m	m	

From Table 2 it is seen that A and B account quite well for the observed intensities.

With A and B, Bi and Ti or Bi and Nb would occupy the same point position. This seemed *a priori* unlikely and if it was assumed that Bi_3NbTiO_9 and $PbBi_2Nb_2O_9$ were built up in the same way, arrangements A and B would imply that Pb, Bi and Nb were distributed over one point position, in $PbBi_2Nb_2O_9$. Therefore, although arrangements A and B cannot be excluded from intensity discussions alone, they seem very improbable and will not be dealt with in the following.

⊜ Bi   ● NbTi   ◯ O

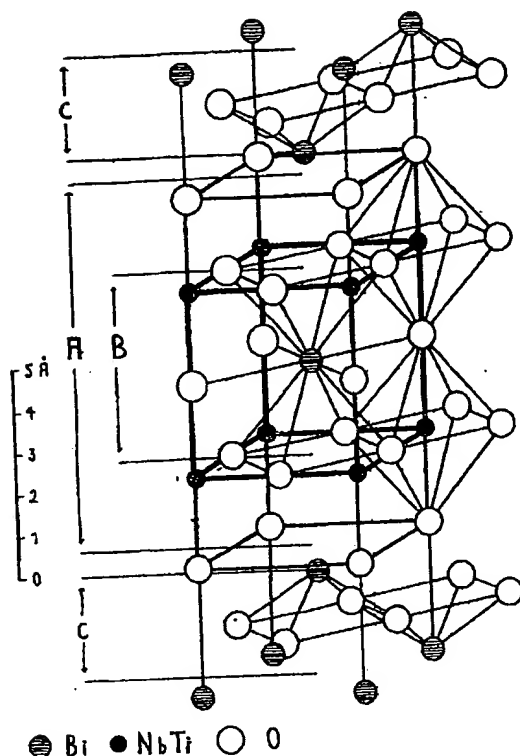Figure 3.

One half of the pseudo-tetragonal unit cell of Bi_3NbTiO_9 (from $z \approx 0.25$ to $z \approx 0.75$). A denotes the perowskitic layer $BiNbTiO_7^-$, C Bi_2O_2 layers and B the unit cell of a hypothetical perowskite structure $BiNb_{0.5}Ti_{0.5}O_3$.

Case C_1'

The following positions were assumed: 4 Bi in 0 0 0, 8 Bi in $\pm$ 0 0 0.396, 8 NbTi in $\pm$ 0 0 0.192. By the same arguments as used for $PbBi_2Nb_2O_9$ the following positions were arrived at:

4 O_1 in 0 0 $\frac{1}{2}$ 8 O_2 in $\pm$ 0 0 0.092   8 O_3 in $\pm$ 0 0 0.268

8 O_4 in $\frac{1}{4}\frac{1}{4}z$; $\frac{1}{4}\frac{1}{4}\frac{1}{2}-z$ $z = 0.164$

8 O_5 in $\frac{1}{4}\frac{1}{4}z$; $\frac{1}{4}\frac{1}{4}\frac{1}{2}-z$ $z = -0.164$.

In Table 3 the intensities are calculated from these parameters.

Case C_2'

4 Bi in 0 0 0, 8 Bi in $\pm$ 0 0 0.200 and 8 NbTi in $\pm$ 0 0 0.412 were assumed. In case 2' (see $PbBi_2Nb_2O_9$) the parameters for the oxygen atoms would be 4 O_1 in 0 0 $\frac{1}{2}$, 8 O_2 in $\pm$ 0 0 0.324, 4 O_5 in $\frac{1}{4}\frac{1}{4}\frac{1}{4}$,

4 O_6 in $\frac{1}{4}\frac{1}{4}\frac{3}{4}$, 8 O_4 in $\frac{1}{4}\frac{1}{4}z$; $\frac{1}{4}\frac{1}{4}\frac{1}{2}-z$ $z = 0.088$

8 O_3 in $\frac{1}{4}\frac{1}{4}z$; $\frac{1}{4}\frac{1}{4}\frac{1}{2}-z$ $z = -0.088$

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Table 3
Weissenberg photographs of Bi_3NbTiO_9

Zero layer

$00l$	$I_{C_1'}$	$I_{obs.}$	$I_{C_2'}$
4	13	m	36
6	0.5	w	10
8	48	m	16
10	310	st	330
12	46	w	.12
14	38	m+	59
16	2.6	w	29
18	100	m+	48
20	240	st	240
22	12	—	0.5
24	42	m	140
26	29	w	42
28	100	m	35
30	190	m	150

$10l$	$I_{C_1'}$	$I_{obs.}$	I_{C_2}
1	2.0	st	17
3	29	m	5.3
5	270	vst	300
7	17	—	1.2
9	29	m	56
11	5.8	w	15
13	49	vw	28
15	270	st	270
17	5.3	—	0.6
19	44	w	92
21	16	w	38
23	110	m	46
25	200	m+	200
27	4.4	—	1.2
29	65	m	110
31	41	m	76

$20l$	$I_{C_1'}$	$I_{obs.}$	$I_{C_2'}$
2	18	vw	2.9
4	12	m+	37
6	0.1	m	16
8	48	m	17
10	300	st	320
12	33	vw	5.8
14	37	w	58
16	2.6	—	31
18	100	vw	45
20	240	m+	240
22	12	—	0.5
24	42	m	140
26	29	m	45
28	100	m+	35

First layer

$21l$	$I_{C_1'}$	$I_{obs.}$	$I_{C_2'}$
1	2.6	m+	22
3	35	vw	6.3
5	290	vst	300
7	19	—	1.0
9	27	m	55
11	3.6	w	18
13	52	w	26
15	270	w	270
17	6.8	—	0.8
19	45	w	90
21	14	w	40
23	110	m	46
25	200	m+	200

$11l$	$I_{C_1'}$	$I_{obs.}$	$I_{C_2'}$
2	34	vvw	2.6
4	2.9	st	41
6	6.8	st	69
8	62	w	22
10	360	st	310
12	14	—	1.0
14	29	vw	76
16	10	vw	40
18	64	w	16
20	250	st	210
22	21	—	0.0
24	66	m	92
26	32	m	61
28	130	m+	27
30	150	m+	200

In T...
from tl...
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With...
$D_{2h}^{23} - m$...
(0 0 0;...

With...
$D_{4h}^{17} - I$...
(0 0 0;...

Val...

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In Table 3 the intensities are calculated with these assumptions.. It is seen from the Table that with C_1' the order of the reflections 101:103, 211:213, 202:204 and 107:109 are reversed. The same result was obtained if the influence of the oxygen atoms was neglected. If z_{Bi} and z_{NbTi} were varied around 0.396 and 0.192 so as to give correct ratios for some of these reflections, large discrepancies occurred for other reflections. With C_2' the intensities turned out to be of the right order. There are however a few discrepancies. 0 0 20 is certainly stronger than 0018 and 0 0 30 > 0028, but the calculated ratios seem to be too large. On the whole the agreement is however good.

Thus if the X ray data for only one of $PbBi_2Nb_2O_9$ or Bi_3NbTiO_9 were considered, different atomic arrangements appeared to be possible, whereas only C_2' seems to explain the observed data both for $PbBi_2Nb_2O_9$ and Bi_3NbTiO_9. With orthorhombic description the positions will be:

$D_{2h}^{23} - mmm$

$(0\,0\,0;\; 0\,\tfrac{1}{2}\,\tfrac{1}{2};\; \tfrac{1}{2}\,0\,\tfrac{1}{2};\; \tfrac{1}{2}\,\tfrac{1}{2}\,0)\; +$

4	Bi_1	(Me_1)	in	4 (a)	$0\,0\,0$
8	Bi_2	(Me_2)	in	8 (i)	$\pm\,0\,0\,0.200$ (0.202)
8	NbTi	(Nb)	in	8 (i)	$\pm\,0\,0\,0.412$ (0.412)
4	O_1		in	4 (b)	$0\,0\,\tfrac{1}{2}$
8	O_2		in	8 (i)	$0\,0\,0.324$ (0.324)
8	O_3		in	8 (f)	$\tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{1}{4};\; \tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{3}{4}$
16	O_4		in	16 (j)	$\tfrac{1}{4}\,\tfrac{1}{4}\,z;\; \tfrac{1}{4}\,\tfrac{1}{4}\,\bar{z};\; \tfrac{3}{4}\,\tfrac{1}{4}\,z;\; \tfrac{1}{4}\,\tfrac{3}{4}\,\bar{z}$

$z = 0.088.$

With pseudo-tetragonal description the positions will be:

$D_{4h}^{17} - I\,4/mmm$

$(0\,0\,0;\; \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})\; +$

2	Bi_1	(Me_1)	in	2 (a)	$0\,0\,0$
4	Bi_2	(Me_2)	in	4 (e)	$\pm\,0\,0\,0.200$ (0.202)
4	NbTi	(Nb)	in	4 (e)	$\pm\,0\,0\,0.412$ (0.412)
2	O_1		in	2 (b)	$0\,0\,\tfrac{1}{2}$
4	O_2		in	4 (e)	$\pm\,0\,0\,0.324$ (0.324)
4	O_3		in	4 (d)	$0\,\tfrac{1}{2}\,\tfrac{1}{4};\; \tfrac{1}{2}\,0\,\tfrac{1}{4}$
8	O_4		in	8 (g)	$\pm\,(0\,\tfrac{1}{2}\,z;\; \tfrac{1}{2}\,0\,z)\quad z = 0.088.$

Table 4

Values of the tolerance factor, t, for different compounds having the $CaBi_2Nb_2O_9$ structure.

Compound	$t.\,100$
Bi_3NbTiO_9	91
Bi_3TaTiO_9	91
$CaBi_2Nb_2O_9$	91
$SrBi_2Nb_2O_9$	99
$SrBi_2Ta_2O_9$	99
$BaBi_2Nb_2O_9$	106
$PbBi_2Nb_2O_9$	101
$NaBi_5Nb_4O_{18}$	91
$KBi_5Nb_4O_{18}$	97

$I_{C_1'}$

22
6.3
300
1.0
53
18
26
270
0.8
90
40
46
200

$I_{C_2'}$

2.6
41
69
22
310
1.0
76
40
16
210
0.0
92
61
27
200

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Table 5

Powder photographs of $CaBi_2Nb_2O_9$ and $SrBi_2Nb_2O_9$. Cr K radiation. Pseudo tetragonal indices.

$CaBi_2Nb_2O_9$

h k l	$I_{obs.}$	I_α	I_β	I_γ
0 0 6	—	8.4	0.8	0.01
0 0 8	m	61	9.6	0.6
1 1 4 + 0 0 10	(m)	230	230	230
0 0 12	—	0.5	19	47
0 0 14	vw	29	46	56
0 0 16	vw	2.6	0.6	4.0
0 0 18	w	100	34	13
1 0 1	—	1.2	0.5	2.9
1 0 3	st	36	1.4	1.4
1 0 5	vst	200	200	200
1 0 7	w	21	0.3	7.8
1 0 9	vvw	18	32	43
1 0 11	—	7.0	0.2	0.5
1 0 13	m+	79	19	4.4
2 0 10 + 1 0 15	(st)	160	160	160
2 1 11 + 1 0 17	(w)	22	0.2	9.0
1 1 2	—	26	0.04	4.8
0 0 10 + 1 1 4	(m)	4.4	14	22
1 1 6	w	4.4	17	26
1 1 8	m	69	13	1.7
2 0 4 + 1 1 10	(st)	200	200	200
1 1 12	—	22	0.1	8.4
1 1 14	w	41	61	72
2 0 2	w	27	0.1	4.4
1 1 10 + 2 0 4	(st)	3.6	13	20
2 0 6	w	3.2	0.04	1.4
2 1 5 + 2 0 8	(st)	59	9.0	0.5
1 0 15 + 2 0 10	(st)	220	220	220
2 0 12	vw	1.4	15	41
2 1 1	w	0.1	2.3	6.3
2 1 3	w	38	2.0	1.0
2 0 8 + 2 1 5	(st)	210	210	210
2 1 7	—	21	0.3	7.8
2 1 9	vvw	18	33	43
1 0 17 + 2 1 11	(w)	4.4	0.01	1.4

$SrBi_2Nb_2O_9$

h k l	$I_{obs.}$	I_α	I_β	I_γ
0 0 6	—	3.2	0.1	0.2
0 0 8	vw	45	11	2.6
1 1 4 + 0 0 10	(m)	260	260	260
0 0 12	vw	0.2	16	35
0 0 14	m	42	58	64
0 0 16	—	0.3	1.4	4.4
0 0 18	w	83	35	18
0 0 20	st	150	160	160

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Table 5 (co

$\beta \, 0\,\overline{0}$

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—

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One half
tioned in
determine
0 0 0.202.
Ca, Sr, Ba
$KBi_5Nb_4O_{1\cdot}$
do not diff
valid for tl
Ca, Sr, Ba

α Only 1
β Rando
γ Only 1

Table 5 (cont.)

$h\,k\,l$	$I_{obs.}$	I_α	I_β	I_γ
1 0 1	—	0.0	2.0	4.0
1 0 3	vw	24	2.0	0.1
1 0 5	st	230	240	230
1 0 7	—	12	0.01	3.6
1 0 9	w	28	42	49
1 0 11	—	2.3	0.01	0.8
1 0 13	m	61	20	8.4
$2\,\theta\,10+10$ 1 5	(st)	190	200	200
$\beta\,00\,20+220+10$ 1 7	(m)	13	0.01	4.0
1 0 19	m	88	110	120
1 1 2	—	16	0.3	1.7
0 0 10+114	(m)	10	20	26
1 1 6	vw	10	22	29
1 1 8	w	52	14	4.4
1 1 10	st	230	240	230
1 1 12	—	13	0.0	3.6
1 1 14	w	56	74	81
1 1 16	—	0.1	4.0	8.4
1 1 18	m	40	10	2.3
2 0 2	—	17	0.4	1.4
2 0 4	—	9.0	19	24
2 0 6	—	0.5	0.6	2.3
$\beta\,11\,14+208$	(w)	43	10	2.3
1 0 15+20 10	(st)	250	260	250
$\beta\,21\,13+20$ 1 2	(vw)	0.01	12	29
2 0 14	w	42	58	64
2 0 16	—	0.2	1.7	4.8
2 1 1	w	0.6	4.8	7.8
2 1 3	w	26	2.6	0.01
2 1 5	st	240	240	240
2 1 7	—	12	0.01	3.6
2 1 9	vw	27	42	49
2 1 11	—	1.2	0.4	2.0
2 1 13	m	59	19	7.8
2 0 10+21 1 5	(st)	190	190	190

One half of the pseudo-tetragonal unit cell is pictured in figure 3. As mentioned in the discussion on $PbBi_2Nb_2O_9$, it was impossible in this phase to determine how Pb and Bi are distributed over the point positions 0 0 0 and 0 0 0.202. It therefore seemed of interest to try to determine the positions of Ca, Sr, Ba and K in the compounds $CaBi_2Nb_2O_9$, $SrBi_2Nb_2O_9$, $BaBi_2Nb_2O_9$ and $KBi_5Nb_4O_{18}$. As the cell dimensions of the Pb, Ca, Sr, Ba and K compounds do not differ much it was assumed that the parameters of $PbBi_2Nb_2O_9$ are also valid for the other compounds. There were three extreme ways of distributing Ca, Sr, Ba and K over the positions 0 0 0 and 0 0 0.202:

α Only Bi in 0 0 202
β Random distribution
γ Only Bi in 0 0 0.

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Table 6 a

Powder photographs of Bi_3NbTiO_9. Cr K radiation.

Orthorhombic indices.

h k l	$10^4 \sin^2 \theta_{calc.}$	$10^4 \sin^2 \theta_{obs.}$	$I_{obs.}$	h k l	$10^4 \sin^2 \theta_{calc.}$	$10^4 \sin^2 \theta_{obs.}$	$I_{obs.}$	h k l	
1 1 1	0914	0909	m	0 2 14	5856⎫	5874	m	1 0 1	
1 1 3	1080	1072	w+	2 0 14	5878⎭			1 0 3	
0 0 8	1333	1319	w+	—	—	5990	vw	0 0 8	
1 1 5	1414	1413	vst	1 3 9	6128	6129	w+	1 0 5	
0 2 0	1774	1767	m+	3 1 9	6172	6175	w+	1 1 0	
2 0 0	1796	1790	m	—	—	6250	vvw	0 0 10	
0 0 10	2083	2078	m	2 2 12	6569	6573	vvw	1 1 4	
2 0 4	2129⎫	2131	w	0 0 18	6747	6747	vw	β1 0 9	
β1 1 9	2136⎭			1 3 11	6961	6961	w	1 1 6	
—	—	2324	vvw	0 4 0	7097⎫	7097	m	1 0 9	
0 2 6	2524	2530	m	0 2 16	7105⎬			β2 0 0	
2 0 6	2546	2546	m	2 0 16	7127⎭			0 0 12	
1 1 9	2580	2585	m	0 4 2	7180⎫	7182	m	1 1 8	
—	—	2739	vvw	4 0 0	7185⎭			1 0 11	
0 2 8	3107⎫	3129	w	β2 4 0	7357⎫	7388	w	2 0 0	
2 0 8	3129⎭			β4 2 0	7420⎬			1 1 10	
1 1 11	3413	3415	w	0 4 4	7430⎭			0 0 14	
—	—	3523	w	2 2 14	7652	7648	w	1 0 13	
2 2 0	3570	3576	st	0 4 6	7847	7836	vw	2 1 1	
2 2 2	3653⎫	3648	vw	4 0 6	7935⎫	8005	w	2 0 8	
β1 1 13	3654⎭			1 3 13	7960⎬			2 1 5	
0 2 10	3857⎫	3860	st	3 1 13	8004⎬			1 0 15	
2 0 10	3879⎭			3 3 1	8054⎭			2 0 10	
0 0 14	4082⎫	4089	w	0 0 20	8330	8330	m		
β1 3 5	4103⎭			1 1 19	8411⎫	8409	m		
—	—	4236	vvw	0 4 8	8430⎭				
2 2 6	4320	4324	w	2 0 18	8543⎫	8558	st		
1 1 13	4412	4414	w	3 3 5	8554⎭				
1 3 1	4462	4454	w-	2 4 0	8887⎫	8888	m		
3 1 1	4506	4504	vw	2 2 16	8901⎭				
β1 1 15	4621⎫	4623	w	4 2 0	8959⎫	8963	m		
1 3 3	4628⎭			2 4 2	8970⎭				
3 1 3	4672⎫	4676	w	1 3 15	9127	9105	st		
β2 2 10	4679⎭			3 1 15	9171	9156	vst		
2 2 8	4903	4896	w	0 4 10	9180	9189	m		
1 3 5	4962	4956	st	4 0 10	9268⎫	9264	m		
3 1 5	5006	5006	st	4 2 4	9292⎭				
1 1 15	5579	5581	st	4 2 6	9709⎫	9712	w		
2 2 10	5653	5652	st	3 3 9	9720⎭				

The intensities were calculated for these possibilities by calculations similar to those for $PbBi_2Nb_2O_9$, and compared with the observed ones. See Table 5. It was found that in no case did γ explain the observed intensities. For the Sr, Ba and K compounds the observed intensities did not permit any decision between α and β. For $CaBi_2Nb_2O_9$, however, only α seemed to give correct intensities. It was therefore concluded that the compounds discussed have the α arrangement.

Table 6 b

Powder photographs of $PbBi_2Nb_2O_9$. Cr K radiation.

Pseudo-tetragonal indices.

h k l	$10^4 \sin^2 \theta_{calc.}$	$10^4 \sin^2 \theta_{obs.}$	$I_{obs.}$	h k l	$10^4 \sin^2 \theta_{calc.}$	$10^4 \sin^2 \theta_{obs.}$	$I_{obs.}$
1 0 1	0889	0892	vw	1 1 14	5682	5699	m
1 0 3	1050	1052	vvw	2 1 9	5974	5990	m
0 0 8	1288	1285	vvw	0 0 18	6520	6529	w
1 0 5	1372	1371	vst	0 0 20	6663 }	6664	vvw
1 1 0	1738	1753	m	1 0 17	6685 }		
0 0 10	2012	2019	m	1 1 16	6889 }	6924	m
1 1 4	2060 }	2068	vvw	β 3 0 5	6903 }		
β 1 0 9	2089 }			2 2 0	6950	6934 }	m
1 1 6	2462	2469	m			6976 }	m
1 0 9	2499	2499	m	2 0 14	7419	7435	m
β 2 0 0	2877 }	2881	m	2 1 13	7744	7749	m
0 0 12	2898 }			3 0 1	7839	7846	vw
1 1 8	3026	3028	w	0 0 20	8049	8052	m
1 0 11	3304	3300	vvw	1 0 19	8133	8131	m+
2 0 0	3475	3475	st	2 2 8	8238 }	8268	vw
1 1 10	3750	3755	st	1 1 18	8258 }		
0 0 14	3944	3946	w+	3 0 5	8332	8339	m+
1 0 13	4269	4270	w+	3 1 0	8688	8673 }	m+
2 1 1	4364	4355	vvw			8690 }	m+
2 0 8	4763	4770	vvw	2 1 15	8872	8874	st
2 1 5	4847	4850	st	2 2 10	8962 }	8980	m
1 0 15	5397	5416	st	3 1 4	9010 }		
2 0 10	5487	5493	st	3 0 9	9449	9450	vvw

The structure of Bi_3NbTiO_9 is thus built up of $Bi_2O_2^{2+}$ layers between which $BiNbTiO_7^{2-}$ layers are inserted. The structure may be looked upon as a perowskite structure where perowskite layers are separated by $Bi_2O_2^{2+}$ layers. This view was supported by the fact that in all cases where the above structure was observed the radii of the ions in the layers lying between the $Bi_2O_2^{2+}$ layers would allow for the formation of a perowskite structure. If the tolerance factor t is calculated from the ionic radii of the elements constituting the layers between the $Bi_2O_2^{2+}$ layers, it is found to lie between the limits 0.9 and 1.1 (see Table 4), the same limits within which perowskite structures are found to be stable.

t was calculated from the formula: $1.06 (R_A + R_O) = 0.95 \ t \ \sqrt{2} \ (R_B + R_O)$. (See (3).)

$$A = (K + Bi)/2 \ Ca, \ Sr, \ Ba \ etc.$$
$$B = (Nb + Ti)/2 \ (Ta + Ti)/2 \ Nb. \ Ta.$$

In the calculations case α was assumed. For calculating t the following values for the ionic radii were used: Bi^{3+} 1.00, Ba^{2+} 1.39, Sr^{2+} 1.20, Ca^{2+} 1.02, Pb^{2+} 1.26, Na^+ 0.97, K^+ 1.33, Nb^{5+} 0.69, Ta^{5+} 0.69, Ti^{4+} 0.66 and O^{2-} 1.36. If, for instance, 1 K + 1 Bi are distributed over one 2-fold position the radius of (K, Bi) was taken as $(r_K + r_{Bi})/2$.

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B. AURIVILLIUS, *Mixed bismuth oxides with layer lattices*

The structure proposed for $CaBi_2Nb_2O_9$ reminds one of the structure of beyerite $CaBi_2O_2(CO_3)_2$ described by LAGERCRANTZ and SILLÉN (4). The unit cell of beyerite is body-centered tetragonal with $a = 3.767$ and $c = 21.690$ Å. The positions of the Ca and the Bi atoms in beyerite are Ca 0 0 0 and Bi $\pm$ 0 0 0.19 (space group D_{4h}^{17}) as compared with $a = 3.860$ $c = 24.87$, Ca in 0 0 0 and Bi in $\pm$ 0 0 0.20 for $CaBi_2Nb_2O_9$.

The "rotating" CO_3^{2-} groups in beyerite correspond to octahedral sheets $Nb_4O_7^{4-}$ in $CaBi_2Nb_2O_9$. Following the notations given by LAGERCRANTZ and SILLÉN (4) the structure described above might also be denoted by X_{11}.

SUMMARY

A series of tetragonal or pseudo-tetragonal phases of general composition $(Bi, Me)_6R_4O_{18}$ have been investigated.

Me: Na, K, Ca, Sr, Ba, Pb.
R: Nb, Ta, Ti.

The positions of the Me and R atoms were determined from the observed intensities and the positions of the O atoms were deduced from space considerations.

The following structure is proposed:

$D_{2h}^{23} - F \, mmm$
$(0 0 0; \ 0 \tfrac{1}{2} \tfrac{1}{2}; \ \tfrac{1}{2} 0 \tfrac{1}{2}; \ \tfrac{1}{2} \tfrac{1}{2} 0) +$

4	Bi	in 4 (a)	0 0 0
8	Bi	in 8 (i)	$\pm$ 0 0 0.200
8	NbTi	in 8 (i)	$\pm$ 0 0 0.412
4	O	in 4 (b)	0 0 $\tfrac{1}{2}$
8	O	in 8 (i)	$\pm$ 0 0 0.324
8	O	in 8 (f)	$\tfrac{1}{4} \tfrac{1}{4} \tfrac{1}{4}; \ \tfrac{3}{4} \tfrac{3}{4} \tfrac{1}{4}$
16	O	in 16 (j)	$\tfrac{1}{4} \tfrac{1}{4} z; \ \tfrac{1}{4} \tfrac{1}{4} \bar{z}; \ \tfrac{3}{4} \tfrac{3}{4} z; \ \tfrac{3}{4} \tfrac{3}{4} \bar{z}$ $z = 0.088.$

From intensity calculations it was found that Ca in $CaBi_2Nb_2O_9$ and Sr, Ba and K in the corresponding compounds are probably situated in the position 0 0 0. The proposed structure is built up of $Bi_2O_2^{2+}$ layers alternating with single perowskite layers. The resemblance to the structure of beyerite is pointed out.

REFERENCES. 1. Internationale Tabellen zur Bestimmung von Kristallstrukturen, Berlin 1935. — 2. Wells, A. F. Z. Krist. *96*, 451, 1937. — 3. Stillwell, Ch. Crystal Chemistry, New York and London, 1938, p. 272. — 4. Lagercrantz, A. and Sillén, L. G. Arkiv Kemi etc. *25*, N:o 20, 1948.